

SENSING IMPACTS OF THE FATE OF TRACE EXPLOSIVES SIGNATURES UNDER ENVIRONMENTAL CONDITIONS

Michelle L. Clark*, Matthew J. Aernecke, Kerin E. Gregory, Dennis E. Hardy and Roderick R. Kunz
Lincoln Laboratory, Massachusetts Institute of Technology
Lexington, MA 02420

Augustus Way Fountain III
Edgewood Chemical Biological Center
Aberdeen Proving Ground, MD 21010

ABSTRACT

A fundamental understanding of the environmental fate and contributing mechanisms of explosives degradation is crucial for determining if emerging explosives sensor systems and concepts of operations are likely to provide effective capabilities since explosive residues vary on tactically relevant timescales. In support of trace explosives detection and sensor development, the temporal persistence and compositional evolution of trace military grade explosives were studied under both hot arid and mild temperate climate conditions as surrogate operational scenarios. The results indicate that for trace (<10 microgram) residues exposed to hot arid conditions in full sun, the half-life is 0.2-5 hours for TNT and 2-100 hours for RDX, while preliminary results for residues exposed to mild temperate conditions in partial sun, the half-life is 2-40 hours for TNT and on the order of 2 to >10 days for RDX. Degradation in both types of climate conditions are dictated by a combination of sublimation and photodegradation, which leads to the formation of an inhomogeneous mixture of degradations products.

1. INTRODUCTION

The threat posed by concealed improvised explosive devices (IEDs) has led to an ongoing nationwide effort to develop means to detect both them and their perpetrators. Among the variety of technologies being pursued to address this challenge are chemical sensors. Successful use of chemical sensing to find an IED is predicated on the understanding that most, if not all types of IEDs, as well as those who handle them, present unique and sufficiently abundant chemical signatures to allow for real-time detection. Although this premise is, in the most general sense true, it underscores the need to thoroughly understand the "signature science" within the various operational environments as a means to better understand the projected capabilities, or lack of capabilities, expected from sensors that rely on chemical signatures. An understanding of the signature science is also needed to guide the establishment of the most effective operational concepts, some of which would be impossible to imagine

without detailed signature knowledge. Signature science studies require statistically significant measurement of the abundance, composition, location, persistence, fate, and background levels of the trace chemical residues. Only when all this information is known, can a sensor model be developed to project its expected capabilities. Therefore, signature science studies must be done in parallel with the sensor development efforts in order to maximize the benefits of the investments made in chemistry-based counter-IED technologies.

With an eye toward these goals, the Joint Improvised Explosive Device Defeat Organization (JIEDDO) and Army Technology Objective has supported the teaming of the U.S. Army Edgewood Chemical and Biological Center (ECBC) with the Massachusetts Institute of Technology's Lincoln Laboratory (MITLL) to investigate the signature science of the current IED problem set. This collective effort, has developed new analytical methods for both conventional (Oyler 2008; Gregory 2009; Kunz 2009c) and homemade (Ginter 2009; Tokarz 2009; Tokarz 2009a) explosives tailored for these signature studies, has determined background explosive levels and spatial correlation between threats and signatures (Kunz 2008; Kunz 2009), and has measured signatures' temporal persistence. (Kunz, 2009a; Kunz 2009d) The environmental persistence drives the timeliness and actionability of all trace explosive observations and was the focus of the FY2008 effort. (Kunz 2009a) This paper describes results from the latest effort comparing the compositional fate of trace signatures of TNT, Composition B (Comp B), and C-4, under hot arid and humid temperate conditions. This study describes the degradation mechanisms and fate of these signatures and is motivated by concerns regarding their detection. As the signature ages and degradation products begin to dominate its composition, the ability for sensors to detect the signature can be affected as well. Ideally, sensors should be able to detect not only the explosive compounds but all of their degradation products as well. This, however, cannot be possible until the products are first identified.

Report Documentation Page				Form Approved OMB No. 0704-0188	
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 2010		2. REPORT TYPE		3. DATES COVERED 00-00-2010 to 00-00-2010	
4. TITLE AND SUBTITLE Sensing Impacts of the Fate of Trace Explosives Signatures Under Environmental Conditions				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Edgewood Chemical Biological Center, Aberdeen Proving Ground, MD, 21010				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution unlimited					
13. SUPPLEMENTARY NOTES To be presented at The 27th Army Science Conference (ASC), sponsored by the Assistant Secretary of the Army (Acquisition, Logistics and Technology), will be held at the JW Marriott Grande Lakes, Orlando, Florida, November 29 - December 2, 2010.					
14. ABSTRACT A fundamental understanding of the environmental fate and contributing mechanisms of explosives degradation is crucial for determining if emerging explosives sensor systems and concepts of operations are likely to provide effective capabilities since explosive residues vary on tactically relevant timescales. In support of trace explosives detection and sensor development, the temporal persistence and compositional evolution of trace military grade explosives were studied under both hot arid and mild temperate climate conditions as surrogate operational scenarios. The results indicate that for trace (<10 microgram) residues exposed to hot arid conditions in full sun, the half-life is 0.2-5 hours for TNT and 2-100 hours for RDX, while preliminary results for residues exposed to mild temperate conditions in partial sun, the half-life is 2-40 hours for TNT and on the order of 2 to >10 days for RDX. Degradation in both types of climate conditions are dictated by a combination of sublimation and photodegradation, which leads to the formation of an inhomogeneous mixture of degradations products.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT Same as Report (SAR)	18. NUMBER OF PAGES 8	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

The focus of the current study was to monitor the quantity and composition of detectable compounds over a period of five days from samples of military-grade explosives (C-4, Comp B and TNT) on painted car metal and inert Teflon® substrates during exposure to dry, full sun conditions in July at Yuma Proving Ground (Yuma, AZ) and to humid, partial sun conditions in April at MIT Lincoln Laboratory (Lexington, MA). This study reports the mass changes of the parent compounds and compositional evolution that occur during sublimation, thermal- and photo-degradation of military grade explosives and characterizes these degradation products for use as potential trace detection targets. Quantitative degradation analysis of the parent compounds, TNT and RDX, was performed using Gas Chromatography-Electron Capture Detection (GC-ECD), and semi-quantitative high resolution accurate mass detection via Direct Analysis in Real Time™ Time-of-Flight Mass Spectrometry (DART-TOF-MS).

2. EXPERIMENTAL METHODOLOGY

2.1 Sample Preparation and Exposure to the Environment

Each test sample used for this study was comprised of 10 µg of a single explosive material placed upon a small test substrate. Two different test substrates were used, the first was a one-by-three centimeter portion of painted-metal car panel and the second was a one-by-three centimeter piece of Teflon® (polytetrafluoroethylene). Sample cutting was performed by a water-jet and the samples were degreased and washed in hot water and soap before use. The explosive materials were applied to these substrates by drop casting 10 µL of solutions in ultra-pure acetone (>99.9%, Aldrich Chromasolv® Plus grade). The drop-casting solutions were 1-mg/mL solutions containing the TNT, Composition B, and C-4, respectively. All energetic materials used in this study were obtained from Accurate Energetic Systems, LLC of McEwen, TN

The substrates were exposed to the ambient environment by mounting them on boards (see Fig 1) that were tilted 20° off normal toward the south. A summary of the meteorological conditions at both locations is given in Table 1. Note that the peak temperature in Yuma was 117 °F with a maximum solar irradiance of 1058 W/m² while in Lexington, the peak temperature was only 80.9 °F and the maximum solar irradiance was 822 W/m². Additionally, the conditions in Lexington were far more humid with a peak humidity of 100% compared to Yuma at 49%.



Fig 1. Photos of the Yuma Proving Ground test area and the test panels (top) as well as the Lexington, MA, test area and coupons mounted on Teflon® boards (bottom).

Table 1. Meteorological Summary of Yuma, AZ, and Lexington, MA

	Yuma			Lexington		
	Min	Max	Avg	Min	Max	Avg
Temperature (°F)	86	117	101	38	81	57
Humidity (%)	12	44	25	7	100	60
Solar Irradiance (W/m ²)	0	1058	290	0	822	220
Wind Speed (MPH)	0	31.1	18.7	0	18.7	2.9

2.2 Sample Extraction

At the designated collection time, each car metal and Teflon® sample tile was collected from the mounting boards, placed in a barcoded 20-mL screw-top amber borosilicate glass vial with a Teflon® resin silicone-lined cap, and shipped with freezer packs to MITLL for extraction and analysis. Samples were extracted the same day as received. A 10-second acetone-rinse method was developed to remove soluble analytes from both surfaces. Each sample tile was removed from the collection vial with a pair of clean metal tweezers. A 10 mL aliquot of CHROMASOLV® Plus HPLC-grade acetone was dispensed on the wide surfaces of the sample tile and collected in the original sample vial. The sample extracts were then concentrated to a few microliters using a TurboVap® LV Concentration Evaporator Workstation under a nitrogen purge stream in a 50 °C water bath and reconstituted with CHROMASOLV® HPLC-grade acetonitrile to 500 µL volume. The sample volume was split into two sample vials containing 250 µL inserts and

capped with Teflon® lined caps for analysis via GC-ECD. All samples were stored in a 5 °C freezer.

2.3 Analysis Methods

2.3.1 Gas Chromatography with Electron-Capture Detection

A modified EPA Method 8095 (EPA 2000) described in detail elsewhere (Kunz 2008) was used for quantitative explosives analysis by GC-ECD. In brief, an Agilent 6890 Gas Chromatograph equipped with two columns and two micro-electron capture detectors was used for this procedure. Each set of two identical samples were run simultaneously on the two parallel GC columns, using a refrigerated (<8 °C) 100-vial autosampler and two parallel auto-injectors. Column 1 (Restek 562719) was a 6-m Restek Rtx-TNT1, 0.53-mm bore, 0.5- μ m film thickness column, while Column 2 (Restek 562885) was a 6-m Restek Rtx-440, 0.53-mm bore, 0.5- μ m film thickness column. Each column was connected to a 12-inch section of 0.53-mm-bore Restek Rxi guard column (Restek 10073) which was replaced periodically as the sensitivity of the method decreased from surface passivation loss. The temperature ramp for simultaneous analysis with the column pair was as follows: hold 90°C for 1 min, ramp at 30°C/min to 120°C, ramp 10°C/min to 180°C, ramp 40°C/min to 270°C for a total run time of 12.25 minutes. The helium carrier flow rate was 217 mL/min which provided a linear velocity of 130 cm/sec.

Retention times were experimentally determined and used for identification of each component. The retention time windows used were ± 0.03 minutes. A series of 19 component calibration standards were prepared in HPLC-grade acetonitrile and stored at <4 °C when not housed in the refrigerated autosampler tray. A ten-point calibration was used for each compound using injection masses of 1, 5, 10, 25, 50, 100, 250, 500, 1000, and 2000 pg from 1- μ l injections of the appropriate standard concentrations. Daily calibrations for quantification consisted of nitrobenzene (NB), 2-nitrotoluene (2NT), 3-nitrotoluene (3NT), 4-nitrotoluene (4NT), nitroglycerin (NG), 2,6-dinitrobenzene (26DNT), 1,3-dinitrobenzene (DNB), 2,4-dinitrobenzene (24DNT), 3,4-dinitrobenzene (34DNT), 3,5-dinitrobenzene (35DNT), pentaerythritol tetranitrate (PETN), 2,4,6-trinitrotoluene (TNT), 1,3,5-trinitrobenzene (TNB), 3,5-dinitroaniline (DNA), 4-amino-2,6-dinitrotoluene (4ADNT), 2-amino-4,6-dinitrotoluene (2ADNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), 2,4,6-trinitrophenylmethylnitramine (Tetryl), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX).

The GC-ECD data was calibrated and quantified using the Agilent MSD ChemStation Enhanced Data

Analysis software package (D.03.00.611). A unique software quantification method file was created for each date on which data was collected. All calibration points were best fit with a forced origin quadratic regression using a weighting inverse to the concentration. Retention times were verified and updated, if necessary, after every 5 samples. Calibration standards, test samples, and control samples were all analyzed using the calibrated method for the date of interest. All data files were manually inspected for accuracy with respect to retention time windows, instrumental sensitivity, and integration parameters after which all quantification reports were exported to a comma delimited file for further analysis using a custom written LabView™ program. All data was corrected for analyte recovery and, if necessary, dilution factor.

Based on a thorough study of method performance (Kunz 2009), the compound-dependent limits of detection are in the range of 1-100 ng, with optimal sensitivity for di- and tri-nitro organic compounds (e.g. DNT, TNT, and RDX) and sensitivity near 100 ng for the mono-nitro compounds (e.g. nitrobenzene and nitrotoluene).

2.3.2 Direct Analysis in Real Time™ (DART) AccuTOF™ Mass Spectrometry

Direct Analysis in Real Time™ AccuTOF™ mass spectrometry (DART™-TOF/MS) was employed for high resolution exact mass analysis to identify the constituents on each field sample tile. The DART™ ion source developed by JEOL, USA, Inc. is an atmospheric pressure thermal electron source coupled with an atmospheric pressure ionization (API) time-of-flight (TOF) mass spectrometer. (Cody 2005; Cody 2005; JEOL 2005) Recent developments in API-MS, including DART and desorption electrospray ionization (DESI), allow for direct surface analysis removing the need for sample preparation. The fundamentals of explosives analysis have been published for an electrospray API-MS method using a desorption electrospray ionization (DESI) source employing liquid-based surface analysis developed by R. Graham Cooks. (Cotte-Rodriguez 2005; Takats 2005) Detailed characterization of explosives degradants detected by atmospheric pressure chemical ionization (APCI) by gas-phase DART MS has not been published and is the focus of this portion of the study. Because these experiments were performed without an internal standard and without control of quantitative delivery of ions at atmospheric pressure to the mass spectrometer, this method was used for compound identification and not in support of the quantitative study.

The car metal and Teflon® sample tiles were directly interrogated by a hot (200 °C) helium gas source to generate ions from surface residues, which then entered the TOF MS orifice for exact mass analysis. For explosives analysis, the DART MS was operated in

negative ion mode to produce mass containing species M^- and/or $[M-H]^-$. Spectra were acquired both in the presence and absence of a methylene chloride dopant for Cl-adduct formation. The addition of chloride ions into the ionization stream prior to MS analysis has been documented to promote detection of RDX via $[RDX+Cl]^-$ adduct formation. (Cotte-Rodriguez 2006; Szakal 2009) Poly(ethylene glycol) (PEG, MW 600) in methanol was used as a mass calibrant. The mass spectra for blank substrates were recorded both with and without methylene chloride, which were later used to subtract background masses from the materials. The mass spectrometer scanned 100–600 m/z at one second intervals.

DART MS data was calibrated, background-corrected, and exported using TSSPro 3.0® Mass Spectrometer Data System developed by Shrader Analytical and Consulting Laboratories, Inc. A calibration coefficient threshold of $3E-10$ was used for accurate mass analysis.

3. RESULTS

3.1 Time Dependence of Primary Compounds

The decay rate for the parent (i.e., TNT and RDX) explosive traces were determined for each of the three materials on each of two substrates (car panel, Teflon®). The amount of each explosive at 14 exposure times up to four days (~100 hours) was determined. A representative example is shown in Figure 2 and the observed persistence half-lives in hours of TNT and RDX from 10- μ g of TNT, Comp B, AND C-4 for Yuma, AZ, and Lexington, MA are reported in Table 2. The solid line in Figure 2 is an exponential fit, primarily to guide the eye. The reported $t_{1/2}$ values are where the measured mass reached 50% of the original. With greater data density, the half-lives corresponding to the two primary mass-loss processes, photodegradation and sublimation, could be determined. For processes where the degradation is

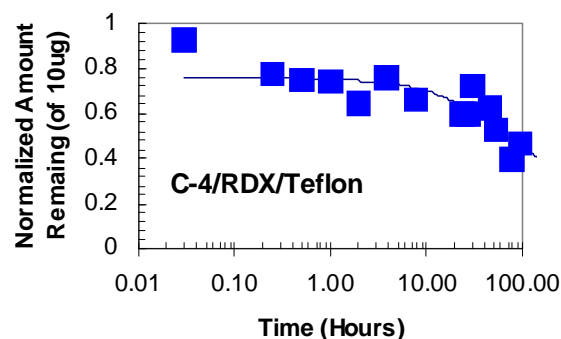


Fig 2. Example of a decay curve showing the amount of RDX remaining on Teflon® deposited from 10- μ g of C-4 for Lexington, MA.

Table 2. Observed persistence half-lives in hours of TNT and RDX from 10- μ g of TNT, Comp B, AND C-4, for Yuma, AZ, and Lexington, MA

	HOT ARID 101°F; RH: 25%	TEMPERATE 57°F; RH: 60%
Explosive	TNT	TNT
Compound	TNT	TNT
Teflon®	5	39
Car Panel	0.5	5.9
Explosive	Composition B	Composition B
Compound	TNT	TNT
Teflon®	0.2	2.6
Car Panel	0.25	3.0
Explosive	Composition B	Composition B
Compound	RDX	RDX
Teflon®	100	228
Car Panel	2	51
Explosive	C-4	C-4
Compound	RDX	RDX
Teflon®	35	>400
Car Panel	2	88

dominated by surface-catalyzed degradation, zeroth-order kinetics have been observed. (Kunz 2009a) .

The results indicate that for trace (<10 microgram) residues exposed to hot arid conditions in full sun, the half-life is 0.2-5 hours for TNT and 2-100 hours for RDX, while preliminary results for residues exposed to mild temperate conditions in partial sun, the half-life is <1 day for TNT and on the order of days for RDX. Note that the half lives are longer for the temperate climate as compared to the hot arid environment. Additionally, the lifetimes observed on the car panel substrates are shorter than those observed for Teflon® since the metal car panels substrates are typically hotter as compared to the Teflon® substrates. Finally note that the TNT half life for

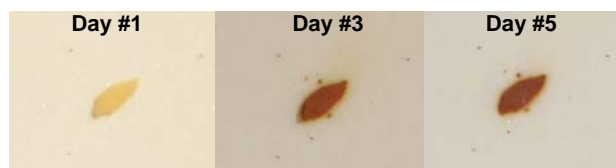


Fig 3. Photographs of a millimeter-scale chip of TNT undergoing photo-oxidation over five days in full sun conditions. This bulk TNT underwent DART-MS analysis as a complement to the studies using 10- μ g samples.

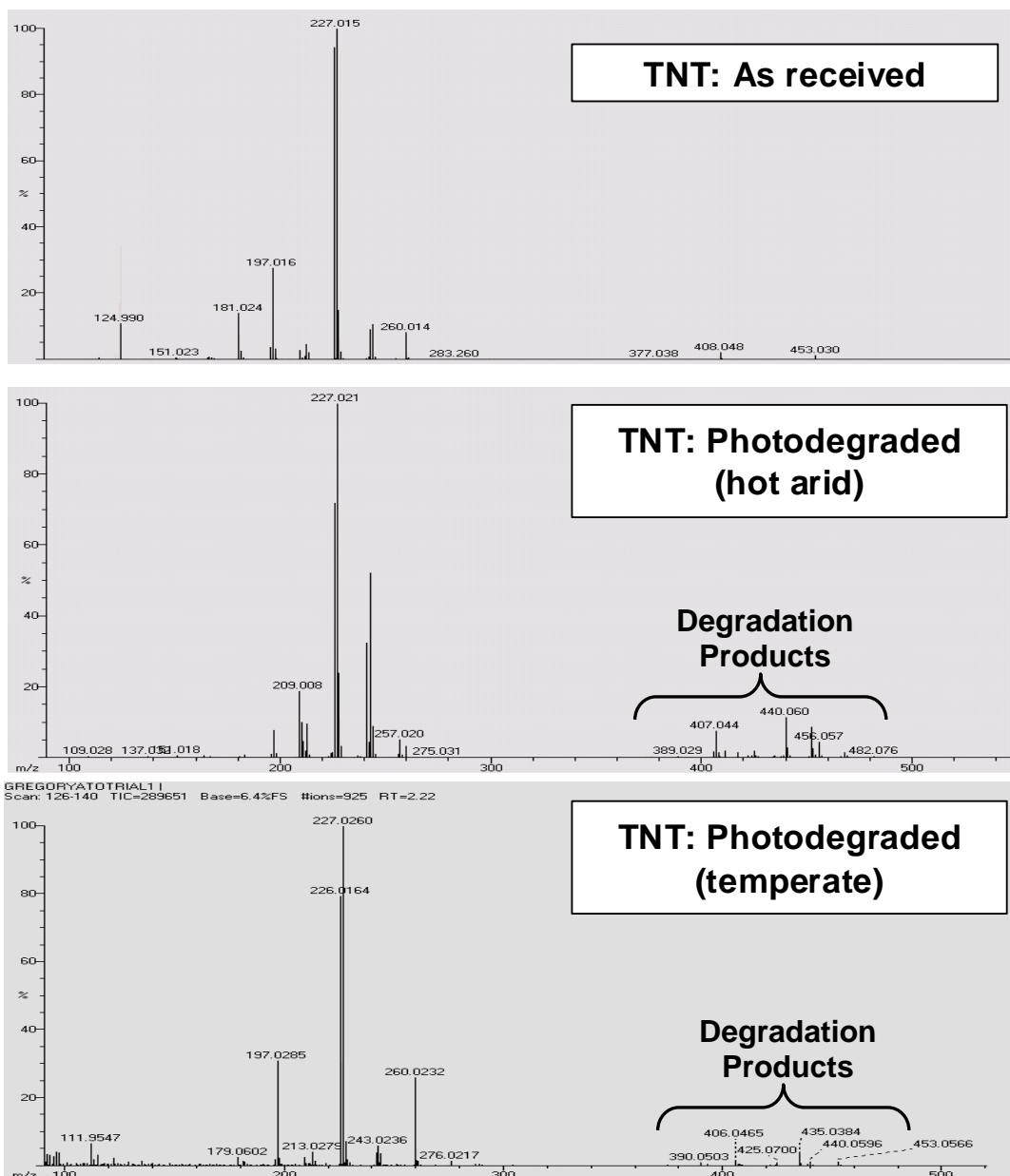


Fig 4. DART™-TOF/MS spectra for bulk TNT unexposed (top) and bulk TNT after photodegradation in Yuma (middle) and Lexington (bottom). Note formation of compounds at high molecular weight (>350 Da). The peaks at 197, 226 and 227, are assigned to TNT while the peaks at 389, 390, 406, 407, 425 and 453 are assigned to TNT dimers and bicylic azo and azoxy (-N=N-) based compounds.

TNT in Comp B is shorter than that of pure TNT and this can be attributed to particle size differences of the TNT in Comp B versus pure TNT.

Degradation in both types of climate conditions are dictated by a combination of sublimation and photodegradation, which leads to the formation of an inhomogeneous mixture of degradations products. After environmental exposure, an observable color change in TNT from pale yellow to red-brown (documented in Figure 3) was further characterized by DART-TOF-MS analysis. The appearance of the documented red-brown

color change is attributed to the compositional evolution of TNT into a mixture of nitro-containing azotoluene, azoxytoluene, and azoxybenzene.

This characterization study also showed evidence that aged TNT polymerizes forming dimers, trimers, and tetramers.

From the DART™-TOF/MS analysis of the material prior to any attempted liquid extraction, 22 different chemicals attributable to TNT were observed in the fully degraded samples. A representative DART™-TOF/MS

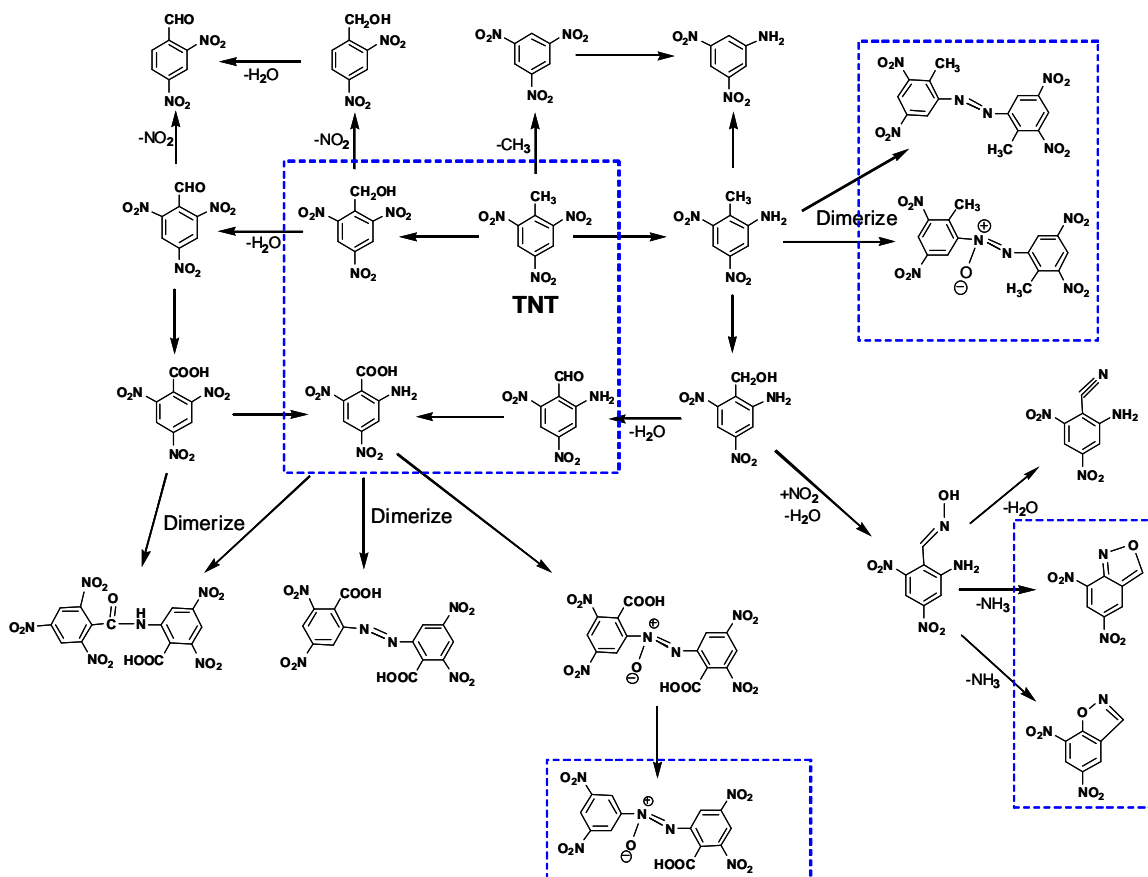


Fig 5. Abbreviated summary of TNT decomposition products. (From Kaplan 1975; Burlinson 1979; Spangoord 1982; Pennington 2007; Robertson 2007). Compounds observed in this work are indicated in the blue dashed boxes.

data for TNT is shown in Figure 4 for bulk TNT unexposed (top) and bulk TNT after photodegradation in Yuma (middle) and Lexington (bottom). Note the formation of compounds at high molecular weight (>350 Da) after exposure to sun. Shown in Figure 5 is an abbreviate summary on TNT decomposition products, many of which were observed by the DARTTM-TOF/MS analysis.

In contrast, RDX was the only compound related to the RDX that was identified in both the C-4 and the Composition B.

These results have direct implications on sensor requirements and performance. Identification of explosives degradation products is essential to sensor development since these compounds which may persist for longer periods of time and provide unique signatures for detection. Furthermore, environmental degradation of trace explosives may impact certain detection methods for which the parent explosive material available for interrogation is rapidly lost or evolves into heterogeneous products to serve as new detection targets. Trace explosive signatures are dynamic, and decrease in

abundance and change in composition on time scales relevant to tactical detection.

4. CONCLUSIONS

Experiments were performed to monitor the abundance and composition of 10- μ g samples of TNT, Comp B, and C-4 left in the open air under hot desert conditions and humid, temperate conditions. These samples were prepared by drop-casting from solution onto car panels and Teflon[®] coupons, resulting in a range of particulate-sizes from 10-50 μ m to aggregates >1 mm. From these measurements, the following observations have been made:

1. Trace amounts of explosives both decrease in abundance and change in composition on a time scale of hours, with half-lives ranging from <1 hour for finely dispersed TNT particulates to >100 hours for aggregates containing RDX. In most instances, less than 10% of the original signature remained after four days. The

observed half-lives are shorter for hot arid climates compared to humid temperate climates.

2. The identified degradation mechanisms for TNT are similar to those previously reported for photolysis in water, with the primary degradation products arising from intermolecular reaction and the formation of insoluble, reddish-brown dimers, trimers, and oligomers linked via azo and azoxy (-N=N-) molecular linkages. At least 20 total degradation products of TNT were identified.
3. No degradation products were identified for RDX, despite strong evidence for its disappearance. Since this material has an exceedingly low sublimation rate, it is assumed that the RDX undergoes degradation into largely gaseous compounds, such as those reported in laboratory studies on the UV degradation of RDX (nitrogen dioxide, nitric oxide, nitrous oxide, formaldehyde, etc.).
4. The compositional changes that occur in TNT particulates are spatially inhomogeneous. The mechanism behind this inhomogeneity is the shallow (<2 μm) penetration depth of UV solar radiation that drives the photodegradation. The result is a highly degraded outer core of the TNT, which surrounds a material core comprised of relatively unreacted TNT. The exact depth of this degraded layer was not measured, but is estimated to be on the order of the penetration depth of the UV radiation.
5. For TNT, sublimation likely contributes to its disappearance, although the fractional mass loss rate due to sublimation is strongly coupled to the particulate morphology, and in particular, the surface-area-to-volume ratio. However, anecdotal evidence was presented to suggest that the formation of the photodegraded "skin layer" acts to slow the sublimation rate.

The results presented in this report support the notion that trace explosive signatures are dynamic, and both decreases in abundance and changes in composition on time scales relevant to tactical detection. Thus, the objective of any successful sensing approach must be to account for, contextualize, or otherwise accommodate these changes in their detection algorithms. Much work still needs to be done, but this represents a start to the process of tailoring detection technologies to the specifics of explosive signatures. Armed with proper information about the signature dynamics, it may be someday possible to determine the age of a signature based on the

compositional distribution of parent and degradation compounds.

ACKNOWLEDGMENTS

This work was sponsored by the U.S. Army/ECBC and JIEDDO/ECBC under Air Force Contract FA8721-05-C-0002. Opinions, interpretations, conclusions and recommendations are those of the authors and are not necessarily endorsed by the United States Government.

The authors also thank Marek Domin (Boston College) for allowing use of the DART MS instrumentation.

REFERENCES

- Burlinson, N. E., Sitzmann, M.E., Kaplan, L.A., and Kayser, E., 1979: Photochemical Generation of the 2,4,6-Trinitrobenzyl Anion, *J. Org. Chem.*, **44**, 3695-3698.
- Cody, R. B., Laramée, J. A., Durst, H. D., 2005: Direct analysis in real time (DART) mass spectrometry, *JEOL News*, **40**, 8-12.
- Cody, R. B., Laramée, J. A., Durst, H. D. ,2005: Versatile new ion source for the analysis of materials in open air under ambient conditions, *Anal. Chem.*, **77**, 2297-2302.
- Cotte-Rodriguez, I., Cooks, R. G. , 2006: Non-proximate detection of explosives and chemical warfare agent simulants by desorption electrospray ionization mass spectrometry, *Chem. Comm.*, 2968-2970.
- Cotte-Rodriguez, I., Takats, Z., Talaty, N., Chen, H., and Cooks, R. G. ,2005: Desorption electrospray ionization of explosives on surfaces: Sensitivity and selectivity enhancement by reactive desorption electrospray ionization., *Anal. Chem.* **77**, 6755-6764.
- EPA (2000), Method 8095: Explosives by Gas Chromatography
- Ginter, J. M., Tokarz, J. A. III, Fountain, A. W. III, Riegner, D., and Kaplan, S. , 2009: Analytical method development for the analysis of homemade explosives by liquid chromatography-mass spectrometry and capillary electrophoresis with diode array detection, *ECBC-TR-681*, Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD 21010-5454.
- Gregory, K. E., Kunz, R. R., Hardy, D. E., Fountain, A. W. III, Ostazeski, S. A., 2009: Quantitative comparison of trace organonitrate explosives detection by GC-MS and (GC-ECD)² methods with emphasis on sensitivity. accepted for publication.
- JEOL, 2005: Application Note MS-0501F: Detection of explosives in muddy water.

- Kaplan, L. A., Burlinson, N.E., and Sitzmann, M.E., 1975: Photochemistry of TNT: Investigation of the Pink Water Problem: Part II, *NSWC/WOL/TR 75-152*, Naval Surface Weapons Center White Oak Laboratory, Silver Spring, MD.
- Kunz, R. R., Clow K.E., Hardy, D., Switkes, M., Krohn K. E., Ostazeski, S. A., Oyler, J. M., Fountain, A. W. III, 2008: Quantitative Analysis of Trace Explosive Residues Found at the National Training Center in Fort Irwin, CA, *ECBC-TR-679*, U.S. Army Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD 21010-5454.
- Kunz, R. R., Clow, K. E., Hardy, D., Krohn, K. E., Fountain, A. W. III, 2009a: Environmental persistence of trace levels of nitro organic explosive materials, *ECBC-TR-683*, Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD 21010-5424.
- Kunz, R. R., Gregory, K. , Hardy, D., Oyler, J., Ostazeski, S. A., Fountain, A. W. III, 2009: Measurement of trace explosive residues in a surrogate operational environment: Implications for tactical use of chemical sensing in C-IED operations. *Anal. Bioanal. Chem.* 395(2): 357-369.
- Kunz, R. R., Gregory, K. E., Hardy, D. E., 2009b: Explosive vapor plumes measured from assembled IED charges, *MITLL 81-1009*, Massachusetts Institute of Technology Lincoln Laboratory, Lexington, MA.
- Kunz, R. R., Gregory, K. E., Hardy, D. E., 2009c: The role of stationary phase selection on performance for explosives analysis using gas chromatography with electron capture detection, *J. Chrom. Sci.*, **48** 310-316.
- Kunz, R. R., Clark, M.L., Gregory, K. E., Hardy, D. E., Fountain, A. W. III, 2009d: The fate of trace explosive signatures in hot arid conditions: implications for their tactical detection I. TNT, Composition B, and C-4, *in press*, Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD 21010-5424
- Oxley, J. C., Smith, J. L., Resende, E., Pearce, E., 2003b: Quantification and aging of the post-blast residue of TNT landmines., *J. Forensic Sci.*, **48**, 1-12.
- Oyler, J., 2008: Rapid quantitative analysis of acetone or acetonitrile extracts of DAAMS tubes, Tedlar bags, soil, and gauze pad extracts for select explosives by gas-chromatography/electron ionization quadrupole mass spectrometry (GC/EI-MS) in selected ion monitoring (SIM) mode, *AM-183*, Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD 21010-5424.
- Pennington, J. C., Thorn, K.A., Cox, L.G. MacMillan, D.K., Yost, S., and Laubscher, R.D., 2007: Photochemical Degradation of Composition B and Its Components, *ERDC/EL TR-07-16*, U.S. Army Corps of Engineers, Engineering Research and Development Center, Vicksburg, MS.
- Robertson, T. J., Martel, R., Quan, D. M., Ampleman, G., Thiboutot, S., Jenkins, T., Provatas, A., 2007: Fate and transport of 2,4,6-trinitrotoluene in loams at former explosives factories. *Soil and Sediment Contamination*, **16**, 159-179.
- Rosencrance, A. B., and Brueggemann, E.E., 1993: Experimental Method for Determination of the Rate of Evaporation of 2,4,6-Trinitrotoluene (TNT) and 2,4-Dinitrotoluene (2,4-DNT), *TR-9122*, U.S. Army Biomedical Research and Development Laboratory, Fort Detrick, MD.
- Sandus, O., Slagg, N., 1972: Reactions of Aromatic Nitrocompounds I. Photochemistry, Project Number 1T061102A32B01, *Technical Report 4385*, Picatinny Arsenal, Dover, NJ.
- Takats, Z., Wiseman, J. M., Cooks, R. G. (2005). Ambient mass spectrometry using desorption electrospray ionization (DESI): Instrumentation, mechanisms, and applications in forensics, chemistry, and biology, *J. Mass. Spectrom.*, **40**, 1261-1275.
- Spangord, R. J., Gibson, B.W., Keck, R.G., Thomas, D.W., and Barkley, J.J. Jr., 1982: Effluent Analysis of Wastewater Generated in the Manufacture of 2,4,6-Trinitrotoluene. 1. Characterization Study. *Environ. Sci. Technol.*, **16**, 229-232.
- Szkal, C., Brewer, T. M. , 2009: Analysis and mechanisms of cyclotrimethylenetrinitramine ion formation in desorption electrospray ionization, *Anal. Chem.* **81**, 5257-5266.
- Takats, Z., Wiseman, J. M., Cooks, R. G. , 2005: Ambient mass spectrometry using desorption electrospray ionization (DESI): Instrumentation, mechanisms, and applications in forensics, chemistry, and biology, *J. Mass. Spectrom.* **40**, 1261-1275.
- Tokarz, J. A. I., 2009: Quantitative analysis of inorganic anions in aqueous samples by ion chromatography with conductivity detection, *AM-184*, Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD 21010-5424.
- Tokarz, J. A. I., Miller, W. E., 2009a: Quantitative analysis of inorganic cations in aqueous samples by ion chromatography with conductivity detection, *AM-198*, Edgewood Chemical and Biological Center, Aberdeen Proving Ground, MD 21010-5454.